

Investigation of Coke Formation in Steam Cracking of Atmospheric Gasoil

Sorood Zahedi Abghari

*Modeling and process control Department, Process Engineering Development Division, Research Institute of Petroleum Industry (RIPI)

Email address: zahedis@ripi.ir

Abstract

To investigate the characteristics of atmospheric gasoil as a suitable feed stock of steam cracker processes, several experiments were designed and carried out in a pilot plant. The operating conditions of the designed experiments were coil outlet temperature (COT), feed flow rate and steam ratio (STR). A group of these experiments were conducted to determine the coke formation rate. Central composite design methodology was utilized to set the experiments and analysis the results. Some statistical tests were used for confirmation of the accuracy, consistency and reproducibility of experimental results. Moreover, statistical model was utilized for investigation of the coke formation rate. To determine the yield distribution of main products a reaction network consists of 21 reactions together with the related kinetic reactions rates were developed. Based on the developed models and utilizing suitable optimization algorithm, the best operating conditions were determined. The results declared that at the 883.9°C as coil outlet temperature, 0.62 as steam ratio and residence time equal to 0.3 sec the optima levels were obtained in which the yield of ethylene, propylene and butadienes were respectively equal to 28.73%, 12.33% and 4.02%.

Keywords

Steam Cracking; Atmospheric Gasoil; Olefins; Modeling; Optimization

Introduction

Olefins are widely used as basic species in production of polymeric material in petrochemical complexes. Ethylene as one of the main light olefins is widely produced in the world. It's globally production was 107 million tones in 2005 and 109 million tones in 2006. By 2010 ethylene was produced by at least 117 companies in 55 countries. To meet the ever increasing demand for ethylene, sharp increases in production facilities are added globally, particularly in the Persian Gulf countries and in China [1]. Over 80% of ethylene is used to produce ethylene oxide, ethylene dichloride and different polyethylenes. Between products, low density and linear poly ethylene are widely demanded

products [2]. Propylene as the other light olefins has been mass produced since sixty years ago. It is used to produce propylene oxide, polypropylenes, propanol and the other related chemicals [3]. Steam cracking process is the main commercial unit for mass production of these olefin species in petrochemical complexes. In this process, gas or liquid hydrocarbons are heated to temperature in the range of 770°C to 870°C. In this range of temperature, the radical reactions are accelerated. These kinds of reactions convert heavy hydrocarbons to lighter ones and the saturated species are converted to unsaturated. The complex mixture is yielded from the proposed reaction network which contains propylene and ethylene. The produced mixture is sent to some separation equipments to separate and purify the valuable produced species.

Coke as one of side product of the process is produced in the secondary steam cracking reactions and settled down in the reactor and TLE (Transfer Line Exchanger). This reduces the heat transfer rate, increases the pressure drop and the possibility of formation of hot spots. The amount of formed coke depends on the feed stock characteristics, operating conditions and the alloy used in the reactor pipe. The amount of contaminated coke on the inner wall of the pipe is increased by passing the time. To lower the effects of coke on the efficiency of the process the reactor temperature are increased. This also increases the coke formation rate and at last it causes to shut down the reactor furnace to clean up [4].

Coke formation is a complex phenomenon which follows from four different mechanisms:

1. Catalytic coke formation
2. Pyrolytic coke formation
3. Condensation mechanism of coke formation
4. Transformation of coke to down streams

In the first step, the heterogeneous reactions are carried out on the metal surface as heterogeneous catalyst of reactor pipes and consequently the filamentous coke is formed [5]. This has the highest rate in comparison with the other coke formation mechanisms while the operating temperature is low and in the range of 500°C to 600°C and the process is at the starting levels. In the pyrolytic coke formation mechanism which is also known as radical coke mechanism, the coke precursors joint to the coke surface and grow the coke [6]. In this mechanism several species as acetylenes, olefins, aromatics and paraffins incorporate in different reactions to form this kind of coke. The highest reaction rates belong to the reactions in which the acetylene is involved and the lowest is for the reactions with paraffins as reactants. The produced coke has amorphous structure [7]. The other steps of coke formation as condensation mechanism and coke transformation are highlighted at the end of reactor while the operating temperature is decreased.

Due to vitality of coke formation in thermal cracking processes, several researchers focused on this subject. The effect of operating conditions as residence time, temperature and partial pressure are investigated by Kunzru and Kumar [8]. Sundram and Froment [9] conducted other research to develop a rigorous model to predict the coke formation. In the proposed model the propylene used as the major coke precursor. The effects of alloys and materials used in the reactor pipes and the coke precursors in gas thermal cracking are studied by Zou et al [10]. Marin & Wauters [11], developed a more precise model to investigate coke formation rate. The proposed reaction network had 14000 reactions and 2400 species for ethane thermal cracking.

To inhibit or to lessen the coke formation, several researchers focused on the coke inhibitors [12-15]. The effect of DMDS as one of the coke inhibitors are studied by Dhuyvetter et al [12]. Moreover, the effect of H_2PtCl_6 as coke inhibitor is studied by Chan et al [13]. The power of Thiophene and benzothiozol to inhibit the formation of coke in thermal cracking of atmospheric gasoil is clarified in the Shubo et al research [14]. Also, the effect of a mixture of components contained Zn, Si and Sulphurous compounds is investigated by Brown et al [15].

In this research, by carrying out several experiments designed and analyzed based on central composite design methodology the effects of different operating

variables on coke formation are estimated. Also, a statistical and a rigorous kinetic model are developed to predict the coke formation rate and the yield of main primary and secondary products. Then the optimization is carried out to determine the optimal point and the best reactor temperature profile.

Experimental Section

Feed Stock Specification

The feed stock of steam cracking pilot plant is an atmospheric gasoil with a boiling range of 218°C to 387°C, with a density of 0.845 gr/cm³. The total sulfur of the feed stock is approximated around 0.75 wt%. The main specifications of this oil cut are listed in Table1.

TABLE 1 THE MAIN PROPERTIES OF THE ATMOSPHERIC GASOIL

Specification	Gas-oil
Nitrogen, Total wt%	<0.5
Hydrogen, Total wt%	13.8
Carbon, Total wt%	85.6
Aromatic Content, vol%	14
Olefin content, vol%	Trace<0.3
Saturate Content, vol%	86
Distillation (D86):	°C
IBP at 760 mm Hg	218
5%Vol. Recovery	257
10%Vol. Recovery	266
FBP at 760 mm Hg	387

Pilot Plant Setup:

The selected experiments were performed in a steam cracking pilot setup that was designed and assembled for steam cracking of the hydrocarbon feed stocks in the range from ethane to vacuum gasoils. The hydrocarbon feed stock and the diluted water are first preheated to the hydrocarbon cracking temperature (approximately 550°C) then mixed together and fed to the reactor in which the main cracking reactions are take place and the reactant mixture are heated up to 860°C. The reactor effluent would be immediately quenched by cooling water in a double pipe heat exchanger. In order to separate the condensate from the gaseous product stream, the

exchanger outlet stream is sent to a flash drum. Then, the gas phase enters a series of condensers, passing through a filter in the final stage.

Experiments

Central composite design methodology was applied to design the experiments. This is used with three design factor, namely, the hydrocarbon feed flow rate(X1), the steam ratio(X2) and coil outlet temperature(X3). The coded level and the natural values of the mentioned variable are clarified in Table 2.

The number of trials was based on the number of design factors and was equal to 19 experiments (15 combinations with four replications). The results of experiments and the design matrix are shown in table3.

As introduced in Table3, the maximum coke formation rate is obtained while the coil outlet temperature, steam ratio and feed flow rate are respectively equal to 1,-1 and -1 in coded level, while minimum coke formation rate is obtained for coil outlet temperature, steam ratio and feed flow rate equal to -1,1 and 1 in coded levels.

TABLE 2 CODED AND NATURAL LEVELS OF THE DESIGN FACTORS.

Design Factors	-1.6818	-1	0	1	1.6818
Feed Flow rate	0.98	2	3.5	5	6.00
Steam ratio	0.4636	0.6	0.8	1	1.13636
Coil Outlet temperature	716	750	800	850	884

TABLE 3 DESIGN MATRIX AND RESULTS OF THE CENTRAL COMPOSITE DESIGN

No	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Feed Flow rate	-1	-1	-1	-1	1	1	1	1	-1.68	1.68	0	0	0	0	0	0	0	-1	-1
Steam ratio	-1	-1	1	1	-1	-1	1	1	0	0	-1.68	1.68	0	0	0	0	0	1	1
Coil Outlet temperature	-1	1	-1	1	-1	1	-1	1	0	0	0	0	-1.68	1.68	0	0	0	1	1
Rate of Coke (gr/cm ² .sec) 10 ⁷	1.67	34.1	0.66	20.9	0.16	18.2	0.03	3.9	12.3	0.51	11.53	0.65	0.06	32.4	1.6	2.35	2.4	24.6	25.6

Modeling Section

Two different models as statistical and rigorous kinetic model are used to investigate the coke formation rate and product yield distribution. The following full quadratic model was used to develop the statistical model. It is obtained by a multiple regression technique for three factors.

$$Y_i = \alpha + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \quad (1)$$

In table 4, the significance of different factors and their interactions, the related coefficient, the ANOVA results for lack-of-fit and the result of R-squared tests have been shown.

This table introduces the significant and insignificant parameters by declaring the p-value. The vital value for "p" is 0.05. The values less than this border point introduce the significant parameters. The insignificant

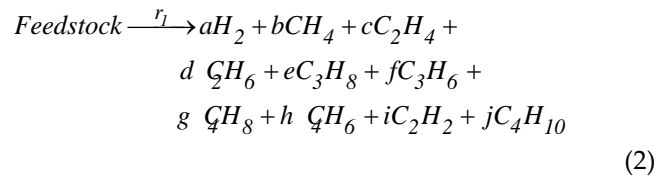
parameters are discarded with a confidence level of 95% while their p-value are higher than 0.05. The p-value of lack of fit is used to determine whether or not the constructed model was appropriate to describe the observed data.

To investigate the yield distribution of main products a molecular reaction network is introduced. Based on the introduced reaction network, reaction mixture is divided into two different sections as primary pyrolysis and dissociation sections. The primary reactions are the only chemical phenomena happened in the first section. However, in the second section the decomposition and polymerization reactions occurred and the primary and secondary reaction product accompanied as the reactants. Pyrolysis-oil which contains several aromatic species is one of the second section reactions products.

TABLE 4 TEST OF SIGNIFICANCE OF FACTORS AND INTERACTIONS FOR STATISTICAL MODEL OF COKE FORMATION, R-SQUARED AND LACK-OF-FIT

Factor or Interaction	Rate of Coke formation * 10 ⁷ (gr/cm ² .sec)		
	Coefficient	T	p-value
Constant	968.57	7.231	0
X ₁	38.013	5.41	0
X ₂	193.05	3.796	0.004
X ₃	-2.92	-8.838	0
X ₁ *X ₁	0.47689	2.093	0.066
X ₂ *X ₂	16.388	2.438	0.037
X ₃ *X ₃	0.002193	10.442	0
X ₁ *X ₂	-0.6494	-0.294	0.775
X ₁ *X ₃	-0.05453	-6.517	0
X ₂ *X ₃	-0.28708	-4.795	0.001
R-Squared	99.10%		
Value of lack of fit	0.073		

To demonstrate the primary reactions, the following pseudo reaction is introduced [16]:



Second part of reactions network contain several reactions to decompose or combine the ten products yielded from reaction demonstrated in equation(2). Table(5) clarifies reactions happens in this section. In this table, EB and B refer to Ethyl benzene and benzene respectively. To consider, other aromatic species a pseudo species "C_{6.5}H₇" is defined. Also "L" refers to pseudo component with 7.5 carbons.

TABLE 5. THE REACTIONS OF SECONDARY SECTIONS IN REACTION NETWORK

Reaction No	Reaction	$A \left(\frac{I}{S} \right)$	$E \left(\frac{kJ}{mol} \right)$
1	$C_2H_6 \leftrightarrow C_2H_4 + H_2$	7.54×10^{13}	273
2	$2C_2H_6 \longrightarrow C_3H_8 + CH_4$	1.87×10^{11}	275
3	$C_2H_4 + C_2H_6 \longrightarrow C_3H_6 + CH_4$	2.57×10^{11}	253
4	$C_3H_8 \leftrightarrow C_3H_6 + H_2$	3×10^{10}	214.7
5	$C_3H_8 \longrightarrow C_2H_4 + CH_4$	1.03×10^{12}	211.8
6	$C_3H_8 + C_2H_4 \longrightarrow C_2H_6 + C_3H_6$	1.267×10^{13}	247.2
7	$2C_3H_6 \longrightarrow 3C_2H_4$	1.636×10^{12}	268.7
8	$2C_3H_6 \longrightarrow 0.3C_{6.5}H_7 + 0.14L + 0.3CH_4$	3.6×10^{10}	208
9	$C_4H_{10} \leftrightarrow 2C_2H_4 + H_2$	3.5×10^{16}	295.9
10	$C_4H_{10} \longrightarrow C_2H_4 + C_2H_6$	1.035×10^{15}	256.6
11	$C_4H_{10} \longleftrightarrow C_4H_8 + H_2$	1.53×10^{14}	261
12	$C_4H_8 \longrightarrow 0.41C_{6.5}H_7 + 0.19L$	1.432×10^5	212.4
13	$C_4H_8 \longrightarrow C_4H_6 + H_2$	1.182×10^{11}	209.3
14	$C_2H_4 + C_4H_6 \longrightarrow B + 2H_2$	8.3×10^2	103.2
15	$C_4H_8 + C_3H_6 \rightarrow T + 2H_2$	1.38×10^4	140.4
16	$C_4H_6 + C_4H_8 \longrightarrow EB + 2H_2$	3.613×10^{12}	246.1
17	$2C_4H_6 \longrightarrow ST + 2H_2$	1.32×10^{12}	263.4
18	$C_2H_4 \longrightarrow 0.15C_2H_6 + 0.233C_3H_6 + 0.1C_4H_8$	3.148×10^{15}	303.8
19	$C_3H_6 + C_2H_6 \longrightarrow C_4H_8 + CH_4$	9.673×10^{13}	291.1
20	$C_3H_6 \longrightarrow C_2H_2 + CH_4$	9	59.38

To determine rate constants as frequency factor and activation energy, least square algorithm was utilized. The objective function clarifies in the equation (3) is used in the algorithm:

$$f = w_1 \sum_i (C_{j\text{model}} - C_{j\text{exp}})^2 + w_2 \sum_i (T_{j\text{model}} - T_{j\text{exp}})^2 \quad (3)$$

$C_{j\text{model}}$ and $C_{j\text{exp}}$ are respectively the reactor outlet molar concentration calculated from model and obtained from experiments. Moreover, $T_{j\text{model}}$ and $T_{j\text{exp}}$ are the temperature of different reactor sections fixed or determined in model and experiments. The procedure of investigation of rate constants is demonstrated in figure (1).

As demonstrated in figure 1, the first step of the procedure is generation the initial estimations. These are the initial estimates of rate constants and activation energies of the proposed reaction network. In the second stage, the reactor model is run with the introduced constants to calculate the outlet concentration of different species. In the next step, utilizing the calculated and experimental information the objective functions are investigated. If the objective functions values meet the minimum value, they are reported as the optimum value. Otherwise, the next generation of rate constants are generated and fed to the other steps of the determination procedure.

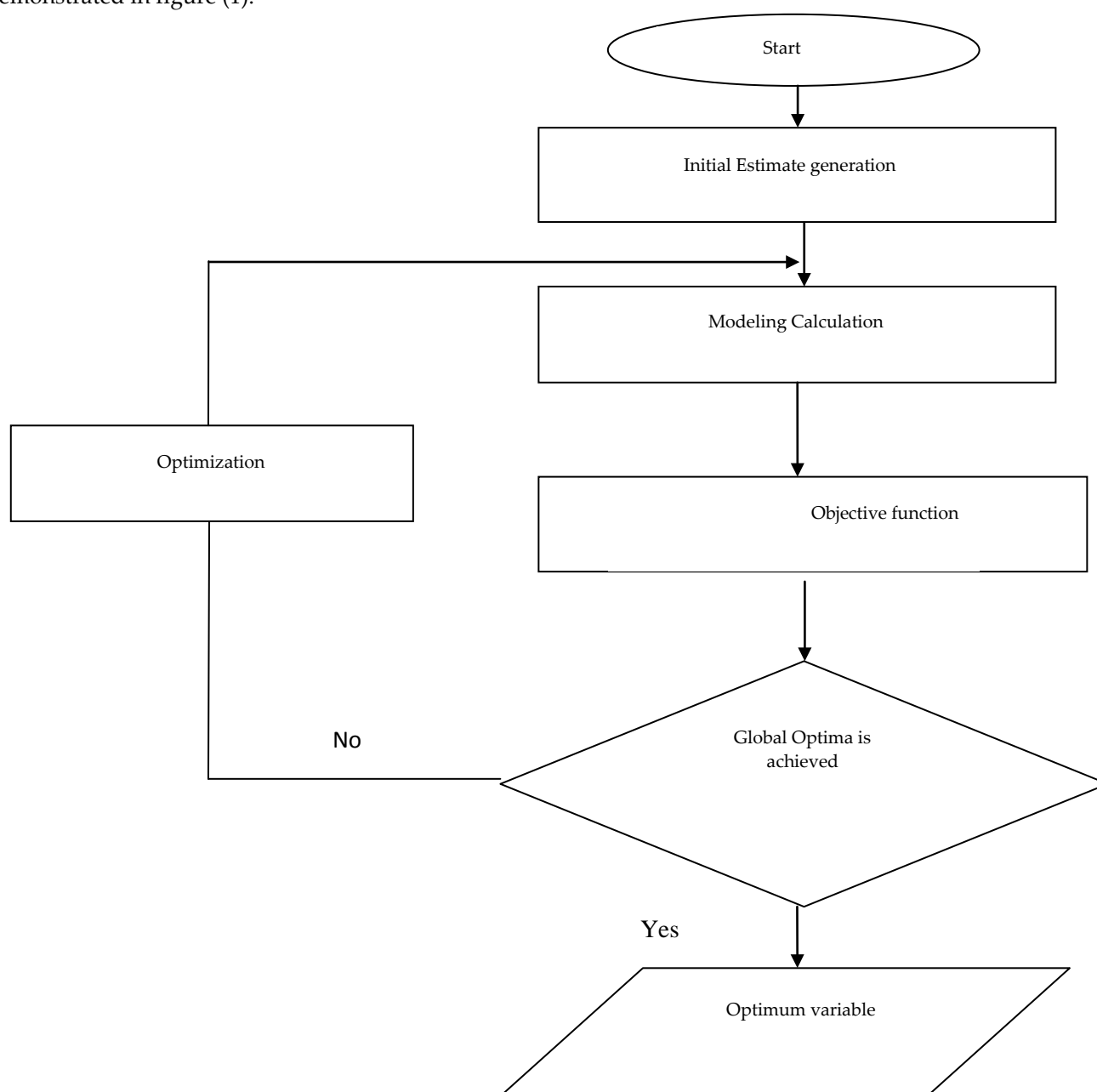


FIG. 1 THE OPTIMIZATION PROCEDURE FOR DETERMINATION OF KINETIC RATE CONSTANTS

Result and Discussion

Based on developed statistical model, the effects of variation of operating variables on coke formation rate are determined and demonstrated in figure(2) to figure(4). In figure(2), the effect of variation of feed flow rate and coil outlet temperature(COT) is clarified. Increasing COT, less than 760(°C) for stable feed flow rate decreases the coke formation rate. On the other hand, an increment in feed flow rate for stable COT decreases the coke formation rate.

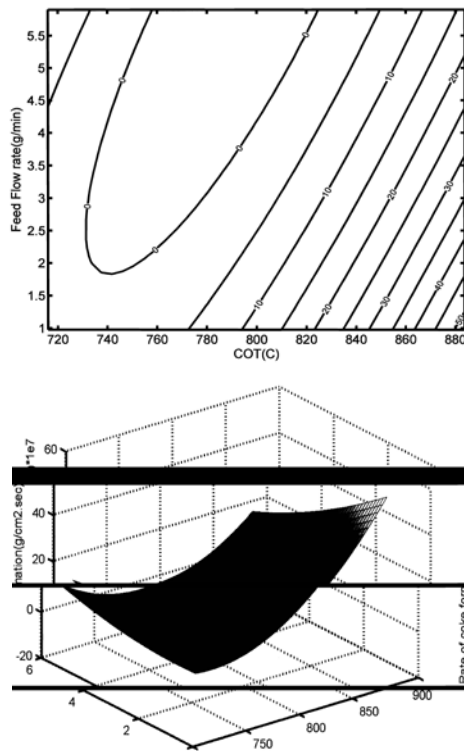


FIG (2) - COKE FORMATION RATE VERSUS FEED FLOW RATE (GR/MIN) AND COIL OUTLET TEMPERATURE (°C) AT CONSTANT STEAM RATIO (GR/GR)

As figure (3) declares, increasing steam ratio with constant operating conditions decreases the coke formation rate. Also, equal increment in steam ratio and COT raises the rate of coke formation with the style like as the position in which only the temperature is increased.

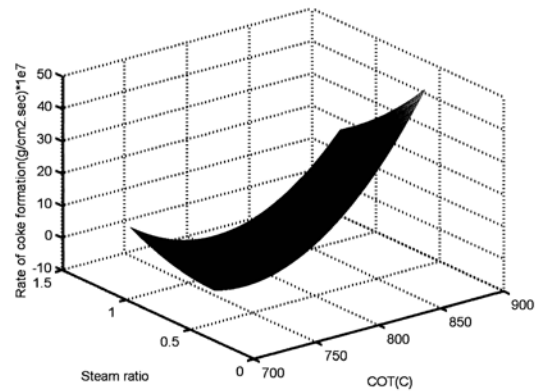
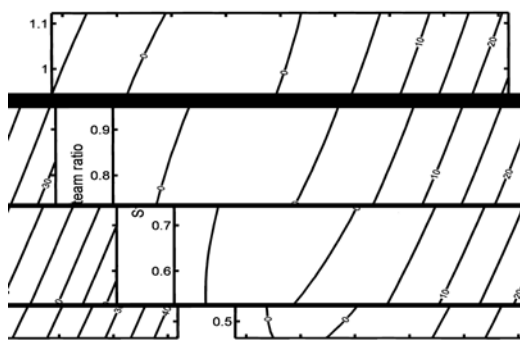


FIG (3) - COKE FORMATION RATE VERSUS COT (°C) AND STEAM RATIO AT CONSTANT FEED FLOW RATE (GR/MIN)

Moreover interaction effect of feed flow rate and steam ratio on coke formation rate can be obtained in figure (4). Indeed, equal increasing of steam ratio and feed flow rate decreases the rate of coke formation.

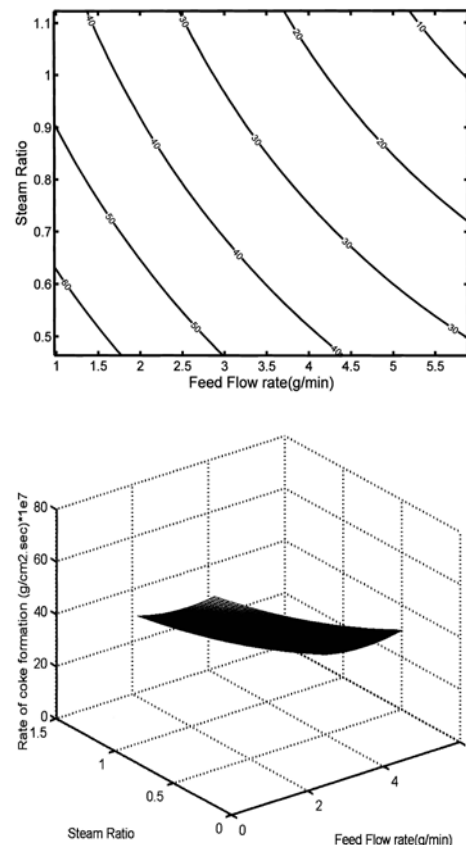


FIG (4) - COKE FORMATION RATE VERSUS STEAM RATIO (GR/GR) AND FEED FLOW RATE (GR/MIN) AT CONSTANT COIL OUTLET TEMPERATURE (°C)

The maximum observable coke formation rate which is equal to 6.62×10^{-6} gr/cm².sec is observed at the maximum coil outlet temperature, minimum steam ratio and minimum feed flow rate which are respectively equal to 884(°C), 0.464 (gr/gr) and 0.977 gr/min.

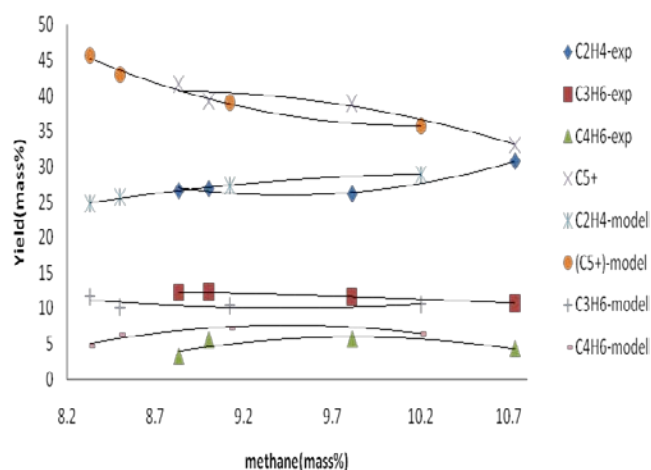


FIG (5) - YIELD OF DIFFERENT PRODUCT VERSUS YIELD OF METHANE

As mentioned above, a molecular reaction network was developed for modeling of steam cracking reactors. Figure (5), demonstrates the effects of the variation of methane yield on the yield of different products. Increasing the yield of methane always decreases the yield of C5+ and increases the ethylene yield. However, the propylene yield has limited variation by increasing the methane yield. Applying the developed statistical and kinetic models together with SQP (Sequential Quadratic Programming) algorithm as a powerful optimization tool, optimization of the pilot plant is conducted. Maximization of net profit of the process is usually suitable objective function in optimization procedure of a chemical process which can be defined as follow:

$$f = \text{income} - \text{cost} \quad (4)$$

In the above equation, the "income" refers to the price of products. Moreover, "Cost" refers to the production cost, in which the cost of coke regeneration, energy consumption during steam cracking and the cost of consumed water are included in production cost.

Hence, the "income" item mentioned in equation (2) should be introduced as follow:

income =

$$6 \cdot 10^{-4} * m_{\text{feed}} * (1.15 * \text{EthyleneYield} + 1.16 * \text{PropyleneYield} + 0.831 * \text{ButadieneYield} + 0.35 * \text{ButenesYield} + 0.266 * \text{FueloilYield} + 0.575 * \text{LightgasYield}) \quad (5)$$

The cost of process refers to the cost of consumed water, cost of feed, cost of heat and consumed energy. Cost of water and feed flow rate are encountered in the following relations:

$$\text{cost} = 2.64 \cdot 10^{-4} * m_{\text{feed}}^0 * \text{steam_ratio} + 0.03156 * m_{\text{feed}}^0 \quad (6)$$

TABLE 6 PRODUCT VALUED AND OPERATING COSTS [17, 18]

Item	Value
Power(\$/kWh)	0.06
Feed(\$/kg)	0.525
Acetylene(\$/kg)	0.95
Ethylene(\$/kg)	1.15
Propylene(\$/kg)	1.16
Butadienes(\$/kg)	0.352
Deionized water(\$/kg)	0.0044
Fuel oil(\$/kg)	0.266
Light gases(\$/kg)	0.574

The cost of consumed energy is divided into two parts as the consumed energy for olefin production and consumed energy for decoking process. The price of consumed energy for production of olefins is calculated by the following equation:

$$P_1 = \frac{0.216}{\eta} * UA * (T_{\text{skin}} - T) \quad (7)$$

In this equation, η , T_{skin} and T respectively refer to the furnace efficiency, skin temperature of reactor pipe and the temperature of reactive mixture. The cost of decoking is calculated by equation (8);

$$P_2 = P_{2C} + P_{2F} \quad (8)$$

P_{2C} is the cost of compressor consumed energy; P_{2F} is the cost of energy consumption in furnace during the decoking procedure. The consumed energy is calculated by the following equation.

$$P_{2C} = 0.216 * Q_{\text{Air}} * P_{\text{outlet}} * \left(\frac{P_{\text{inlet}}}{P_{\text{outlet}}} \right)^{\frac{k''-1}{k''}} * \frac{k}{k-1} \left[\left(\frac{P_{\text{outlet}}}{P_{\text{inlet}}} \right)^{\frac{k''-1}{k''}} - 1 \right] \lambda \quad (9)$$

The P_{2F} variable is defined as follow:

$$P_{2F} = P_1 * \lambda \quad (10)$$

λ is the ratio of decoking over olefin production time periods. The defined optimization problem has some constrained. At first, due to the metallurgical limitation, the reactor temperature should not be

exceeded than 890°C. As the second constrained, the yield of each product have to be in the range of 0% to 100%. And due to the mass continuity rule, the reactor mass inlet flow rate should be equal to the reactor mass outlet flow rate. The result of optimization procedure is calculated and clarified in table7.

TABLE 7 THE RESULT OF OPTIMIZATION

Operating condition	Value
Coil outlet Temperature(°C)	883
Feed flow rate (gr/min)	6.02
Steam ratio(gr/gr)	0.62
Residence time(sec)	0.3
Y _{Acetylene} (%)	1.23
Y _{ethylene} (%)	28.23
Y _{propylene} (%)	12.33
Y _{Butadiene} (%)	4.02
Y _{Butenes} (%)	0.98
Y _{LG} (%)	9.70
Y _{fuel oil} (%)	28.16
Rate of Coke formation (gr/cm ² .sec)*10 ⁷	24.32

Determination of optimum temperature profile in reactor is one of great challenges in running of steam cracking process. Three different temperature profiles for three different optimization cases as maximization of ethylene production, maximization of propylene production and maximization of profit are determined and demonstrated in figure(6).

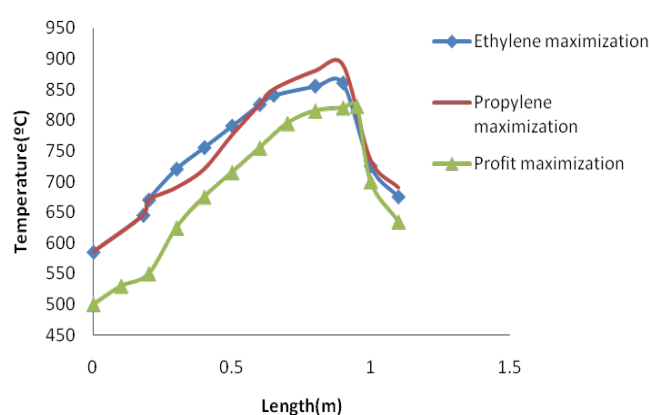


FIG. 6 THE OPTIMUM PROFILE FOR MAXIMIZATION OF PROFIT, PROPYLENE AND ETHYLENE AT RESIDENCE TIME AND STEAM RATIO RESPECTIVELY EQUAL TO 0.362 SEC AND 0.88

As demonstrated in the aforementioned figure, Temperature profiles for two optimization cases which are solved to maximize the yield of propylene and ethylene have many similarities. The reactor inlet and

outlet temperature are same in both profiles. But, the average reactive mixture temperature for ethylene maximization case is greater than for the propylene maximization challenge. Infact, the rate of temperature increment for the first case is greater than for temperature profile of the second case. The maximum point of temperature profile of the second case is greater than the first one. The third one has many differences from the others. The style of these profiles can be interpreted by the nature of production of the two important olefins as ethylene and propylene. These two olefins are the main primary products which contribute in formation of the secondary products. But propylene has greater role and consequently is more consumed in secondary products. Increment the temperature along the reactor with high rate, raises the possibilities of improvement of secondary reactions that will cause to consumed more propylene. So, reduction of the rate of temperature raising at the inlet reactor regions and maximizing the temperature before sharp declining maximized the yield of propylene. But, since ethylene is produced in primary and some secondary reactions, determination of the operating condition to make little improvement in the secondary reactions may maximize the ethylene production. Moreover, the temperature profile for profit maximization shows several differences from the others. The inlet, average value and the outlet temperatures of this profile are less than the others. Infact, the demonstrated profiles declares that the amount of energy consumption has highlighted effect in the profit of the process.

Conclusions

To evaluate the atmospheric gasoil as a suitable feed stock of steam cracking process, several tests were carried out in a pilot plant. Based on the experimental results, a rigorous kinetic and a statistical model were developed. The results of statistical model proposed that increasing the Temperature could increases the rate of coke formation. While increasing the feed flow rate and steam ratio has inverse effect and could decrease the coke formation rate.

Based on rigorous kinetic model and the experimental results, the yield of main products as ethylene, propylene and butadienes versus the yield of methane as an index of improvement of reaction network were studied. While the yield of ethylene shows increasing trends, the style of C₅₊ yield has decreasing trend and propylene has limited variation. The optimization was carried out to determine the best operating conditions

for profit maximization. To develop the related objective function, the price of product is considered as income and the summation of the price of feed, cost of consumed water and cost of consumed energy is considered as the cost of the process. The results clarified that the maximum observable profit is obtained at the COT, Feed flow rate and steam ratio equal to 883°C, 6.02gr/min and 0.62 (gr/gr). To determine the effect of reactor temperature profile on the yield of main products and the net profit, optimization was carried out. The results clarified that energy consumption has important effect on the net profit. Moreover, the rate of temperature increment and the value of maximum temperature have important rolls on the maximization of olefin production.

ACKNOWLEDGMENT

The financial support provided by research and development center of National petrochemical company is highly appreciated.

Nomenclature

COT	coil outlet temperature (°C)
Coef.	coefficient in quadratic model
T _{furnace}	temperature of reactor furnace (K)
T _{skin}	skin temperature of the reactor (K)
XOT	cross over temperature (°C)
X ₁	experimental design parameter (feed flow rate (gr/min))
X ₂	experimental design parameter (steam ratio)
X ₃	coil outlet temperature (°C)
Y _i	yield of products (mass %)
α	constant coefficient in quadratic model
β_{ij}	coefficients in quadratic model
λ	experimental factor for predicting the relationship between decoking time and operating time (hr/hr)

REFERENCES

- Dhuyvetter I., Reyniers M. F., Forment G. F, Marin G.B., the Influence of Dimethyle Disulfide on Naphtha Steam Cracking, 40, 4353-4362, 2001
- "Ethylene Technology, Process, End Use, manufacturers list, global production and consumption "; www.ynfx.com; 2007
- "Ethylene";<http://en.wikipedia.org/wiki/Ethylene>
- F.D. Kopernike, G. Zimmermann, G.C. Reyniers, G.F.Froment," Relative Rates of Coke Formation From Hydrocarbons in Steam Cracking of Naphtha.2.Paraffins,Mono-Di-and Cycloolefins, and Acetylenes", Ind. Eng. Chem. Res.,1993,Vol 32,pp 56-61.
- Formation in Steam Crackers for Ethylene Production" Chemical Engineering and Processing, 2002, Vol.41, pp 199-214.
- F.Shubo, S.Liming, L.Qiangkun; "A Study on Coke deposition and coking inhibitors during AGO Pyrolysis in pulsed micro reactor system"; Journal of analytical and applied Pyrolysis"; vol.65; PP 301-312.
- G.Chan, F.Inal and S. Senkan; "Suppression of Coke Formation in the steam Cracking of Alkanes: Ethane and Propane"; I & EC Research; 1998; vol(37); pp 901-907.
- G.Merz; G.Schmidt; D.Kaufmann;"Cracking furnace fundamentals"; Linde Ethylene Technology Seminar; Bahrain; 2003.
- Haiyang Cai, Andrzej Kizyeicki, Michael C. Oballa," Coke . K.M.Saundram; G.F.Froment; "Modeling of thermal cracking kinetic-II Cracking of Iso-Butane, of n-Butane and of mixtures Ethane-Propane and n-Butane";Chemical Engineering science;1977;vol 32;pp 609-617.
- K.M. Sundaram, G.F. Froment,' Kinetics of Coke Deposition in the Thermal Cracking of Propane", Chemical Engineering Science, 1979, Vol.34, pp 635-644.
- Mohaddecy, R.S., Sadighi, S., Zahedi, S. and Bahmani, M. "LP modeling of Tehran refinery to maximize the net profit", Technical Report, Tehran Refinery (2006).
- "Propylene"; <http://en.wikipedia.org/wiki/Propene>
- R. E. Brown; L. E. Reed; G. J. Greenwood; T. P. Harper; M. D. Sharre; US Patent NO:5565087;(1996).

Renjun Zou; "Fundamentals of pyrolysis in Petrochemistry and Technology"; Lewis Pub; 1993.

S.E.Babash, T.N. Mukhian," Effect Coke Inhibition in Pyrolysis Furnaces", PTQ, Autumn1999, pp 113-120.

Tao Ren, Martin Patel and Kornelis Block; "Energy Efficiency and innovative emerging technologies for olefin production"; European Conference on Energy Efficiency in IPPC; 2005.

"The price of different products",
<http://WWW.nioc.org/publications/fanavari/findex.asp>

Zou Ranjun, Lou Qiangkum, Liu Huicai, N. Fenghui," Investigation of Coke Deposition during the Pyrolysis of Hydrocarbon", Ind. Eng. Chem. Res., Vol, 26, pp 2528-2532.